



# Nucleation and growth of Mg-bearing calcite in a shallow, calcareous lake

Ilona Nyirő-Kósa<sup>a</sup>, Ágnes Rostási<sup>a</sup>, Éva Bereczk-Tompa<sup>a</sup>, Ildikó Cora<sup>b</sup>, Maja Koblar<sup>c</sup>,  
András Kovács<sup>d</sup>, Mihály Pósfai<sup>a,\*</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, University of Pannonia, Veszprém, H8200 Hungary

<sup>b</sup> Institute of Technical Physics and Materials Science, Centre for Energy Research, Budapest, H1122 Hungary

<sup>c</sup> Jožef Stefan Institute, 1000 Ljubljana, Slovenia

<sup>d</sup> Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52428 Jülich, Germany

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## ABSTRACT

Both inorganic and microbial processes play important roles in carbonate mineral precipitation in freshwater lakes. Identifying the individual factors that determine particle size, shape, composition, and the spatial relationships of carbonates with other constituents of the sediment are important for understanding sediment formation and nutrient cycling, and for providing input for lake management planning. We studied the formation of Mg-bearing calcite in Lake Balaton, a large, shallow, Mg-rich, calcareous lake in Hungary, by filtering particles from the water and analyzing them using X-ray powder diffraction and electron microscopy techniques. Mg-bearing calcite particles from Lake Balaton have distinct and remarkably consistent morphologies, independent of seasonal and annual variations in water temperature and composition. They are typically elongated parallel to the [001] crystallographic direction, are about 4 to 8  $\mu\text{m}$  long, and even though appear to be composed of many smaller units, electron diffraction patterns indicate they are perfect single crystals. The Mg content of calcite increases from west to east, reflecting a gradient in lakewater composition. The calcite crystals are invariably attached to nm-scale flakes of smectite, suggesting that the clay mineral serves as a nucleation site. The templated nucleation may direct the growth of calcite parallel to the clay flakes, resulting in its elongated shape and single crystalline character. While in deep, oligotrophic lakes calcite typically nucleates on picoplankton cells, we rarely observe this phenomenon in Lake Balaton. Because of the shallowness of the lake, sediments are stirred up by even moderate winds and the movement of organisms, making nm-scale smectite flakes readily available for templating calcite nucleation. Thus, while calcite precipitation is an indirect consequence of biological activity (photosynthesis), the physical properties of the particles are primarily determined by inorganic factors.

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## 1. Introduction

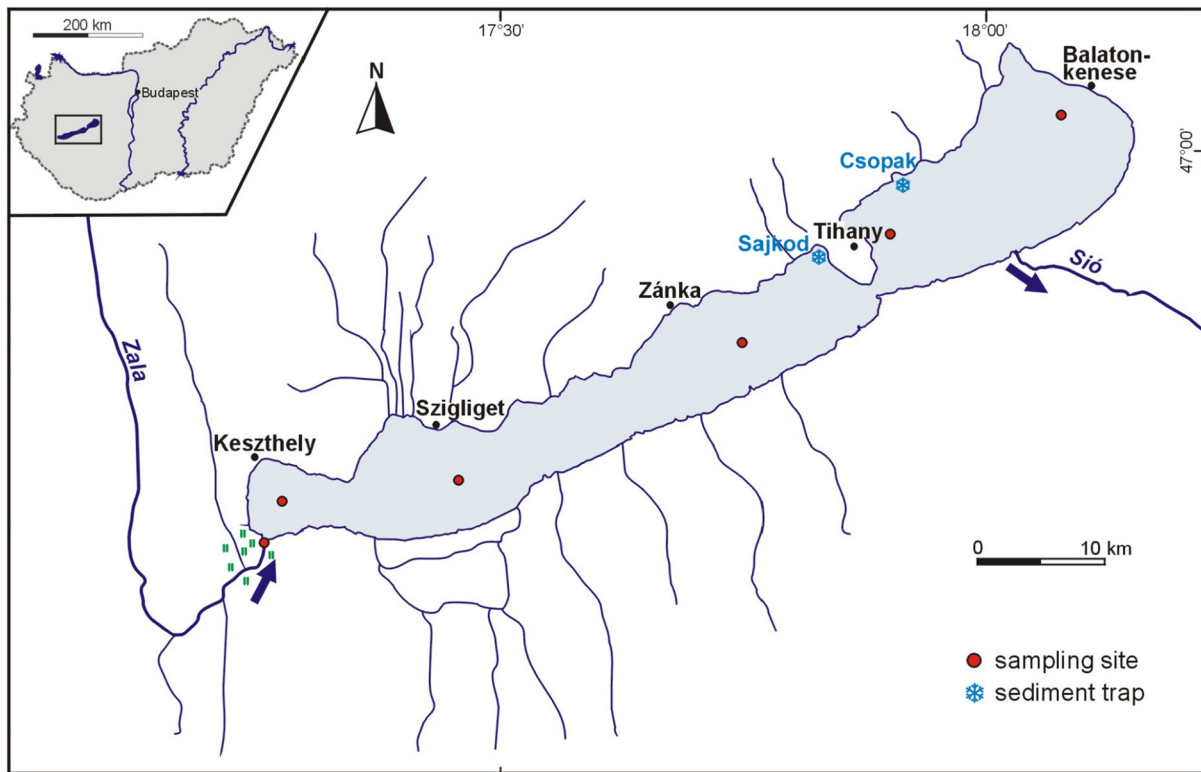
Calcium carbonate minerals are widespread on the surface of the Earth, can form both inorganically and by biological mediation, and are important in the global carbon cycle (Tucker and Wright, 2009); thus, they represent a crucial link between geology and life. Many aspects of the interplay between biology and the formation of inorganic carbonate crystals have been extensively studied, in both marine (Morse et al., 2007) and freshwater environments (Gierlowski-Kordesch, 2010). In this study, we focus on

\* Corresponding author. University of Pannonia, Department of Earth and Environmental Sciences, Egyetem 10., Veszprém, H8200 Hungary.

E-mail address: mihaly.posfai@gmail.com (M. Pósfai).

the precipitation of calcite in a shallow lake. In particular, we study the roles of microorganisms and pre-existing mineral particles in calcite nucleation, the effect of high dissolved Mg content on the composition and structure of calcite, and assess both biogenic and inorganic factors that affect the growth and, consequently, the size and shape of the precipitating crystals.

Biology can play multiple roles in the precipitation of carbonates in lacustrine settings, even in cases where the inorganic crystals are not used by the organism for a function (i.e., we are concerned here with biologically-induced rather than biologically-controlled carbonate mineralization). Firstly, photosynthesis by phytoplankton causes a shift in water chemistry that results in calcium carbonate supersaturation, triggering calcite precipitation (Thompson et al., 1997). Beyond changing the water chemistry, microorganisms can be key physical or chemical mediators of calcite



**Fig. 1.** Lake Balaton, with sampling sites marked where suspended particles were collected (red dots) and two sites where sediment traps were used in February 2012 and January 2017. The flow directions of the Zala river and the Sió canal, the major tributary and the only outflow of the lake, respectively, are also indicated. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

nucleation and also affect the growth of calcite seeds. Cyanobacteria provide suitable surfaces for the heterogeneous nucleation of calcite nuclei by binding  $\text{Ca}^{2+}$  on their surfaces, owing to the presence of extracellular polymeric substances (EPS) (Dittrich and Sibling, 2005; Obst et al., 2009; Schultze-Lam et al., 1996; Stabel, 1986; Zhang et al., 2015), and also affect the growth of the crystals (Benzerara et al., 2006). Seed formation may also be influenced by soluble metabolites that act as inhibitors or nucleation agents (Meldrum and Cölfen, 2008). In addition to the above processes that can be described by classical nucleation theory, calcite nucleation in biological systems often follows 'non-classical' pathways (De Yoreo et al., 2015). For example, the formation of prenucleation clusters in solution, or the deposition of amorphous calcium carbonate (ACC) as a precursor to calcite (Politi et al., 2008), as well as the formation of mesocrystals have been all described for calcite. Mesocrystals represent a special case of superstructure formation, since they are assembled from individual nanocrystals but scatter X-rays like a single crystal (Cölfen and Antonietti, 2005; Kim et al., 2014). Although several mechanisms of mesocrystal formation are known, in natural systems typically organic matrices or biopolymers are responsible for the oriented attachment of the nanoparticles (Bergström et al., 2015; Meldrum and Cölfen, 2008).

The effects of abiogenic controls over calcite nucleation and growth (including temperature, pH, alkalinity,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations) have been extensively studied (Morse et al., 2007; Niedermayr et al., 2013). Among the inorganic influences, the role of dissolved Mg is of particular interest for the present study. Mg is known to be an inhibitor of calcite nucleation, although the exact mechanism of its inhibitory effect remains unclear (Xu et al., 2013). Based on observations of natural systems (Richter et al., 2011), laboratory experiments (Davis et al., 2004; Hong et al., 2016) and atomistic simulations (Titiloye et al., 1993),  $\text{Mg}^{2+}$  can interact with specific crystal faces of calcite, resulting in a vari-

ety of distinct crystal morphologies (Fernandez-Diaz et al., 1996; Meldrum and Cölfen, 2008). Mg can also play a role in phase transformations of calcium carbonate: it was found to stabilize an initially precipitating, Mg-bearing ACC, and then facilitate its conversion to calcite (at Mg/Ca ratios relevant for the present study) (Purgstaller et al., 2016). Based on the amount of Mg incorporated into calcite, various terms are in use, including low-magnesium-calcite (LMC, with <4%  $\text{MgCO}_3$ ), high-magnesium-calcite (HMC, with >4%  $\text{MgCO}_3$ ), and very high-magnesium calcite (VHMC) or 'protodolomite' (Gaines, 1977), to refer to carbonate phases with near dolomite composition ( $\text{CaMg}(\text{CO}_3)_2$ ) but a disordered arrangement of cations (Gregg et al., 2015; Zhang et al., 2010). In this study we discuss calcite particles with a  $\text{MgCO}_3$  content ranging from 2 to ~30 mol%, and for these we use the term Mg-bearing calcite.

Several factors affecting calcite nucleation and growth can be studied in Lake Balaton, a lake of great cultural and economic (touristic) importance in landlocked Hungary. The lake has been a distinguished subject of scientific research for more than a century (Lóczy, 1913). For a surface area of ~600 km<sup>2</sup> the lake is extremely shallow (on average 3.5 m), resulting in the almost continual presence of sediment particles in the water column, stirred up by even relatively mild breezes. The lake has an elongated shape, with its long axis roughly along the W–E direction and is divided into Western and Eastern Basins by the Tihany Peninsula (Fig. 1). Due to the prevailing northerly wind direction, sand-sized particles are deposited along the south shore, whereas silt-sized particles dominate elsewhere in the sediment. Since most tributaries drain carbonate-rich terrain (Triassic limestone and dolomite in the north, young clastic sediments in the south), Balaton is a calcareous lake with a large dissolved Mg/Ca molar ratio, ranging from 1 to 4 (Tompá et al., 2014; Tullner, 2002). The main inflow, the Zala river enters the lake at its western end, while the only outflow, the Sió canal drains it near its eastern end, resulting in

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